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(54) Improved propylene oxide and styrene monomer co-production procedure

Verbessertes Verfahren zur Herstellung von Propylenoxid und Styren

Procédé amélioré pour la préparation du propylènoxide et du styrène

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Description

DESCRIPTION OF THE PRIOR ART

[0001] U.S. patent No. 5,210,354 refers to an improved propylene oxide and styrene co-production procedure. The improvement consists in revaluating heavy sodium-containing residual currents, obtained as a by-product. According to this procedure, the heavy sodium-containing residue is mixed with an aqueous acid, preferably sulfuric acid, in relatively mild conditions, e.g. 20-100°C, preferably 40-90°C. The resulting mixture is separated in immiscible phases, one aqueous phase containing sodium and another organic phase having a limited sodium content. To the organic phase a compatible acid catalyst is added, such as p-toluenesulfonic acid, and the resulting mixture is cracked at high temperature to form 1-phenylethanol and styrene monomer, which products may be separated from the remaining heavy compounds through distillation. Temperatures of 70 to 300°C, preferably 120 to 220°C, and pressures below the atmospheric pressure, such as 100-400 mm. Hg, appropriate for vaporizing the light compounds, are used for the cracking. The cracking products, 1-phenylethanol and styrene, entail an increased performance of the styrene in the course of the process in view that 1-phenylethanol is a styrene precursor. Furthermore, the heavy cracking products are useful as low sodium content fuels. In a most preferred variant of the process, after the acid treatment the organic phase is submitted to vacuum evaporation in a film evaporator designed to separate approximately 40% by weight of a fraction of volatile compounds. This top fraction may be taken directly to the dehydration section of commercial propylene/styrene oxide co-production processes where certain components of the light header fraction are transformed into styrene under the conditions normally applied to 1-phenylethanol dehydration. The heavy film evaporator residues are used as revalued fuel on account of their low sodium content.

[0002] The acid is used in sufficient quantity to react with all the sodium present in the heavy residue. In the event that sulfuric acid is used, a sufficient amount of acid is applied to form sodium sulfate, i.e. less than 0,5 moles of sulfuric acid for each atom gram of sodium and preferably less than 1 mole of sulfuric acid for each atom gram of sodium to form sodium bisulfate.

[0003] U.S. patent No. 5,276,235 refers to an improvement to the procedure described in the preceding patent. A critical aspect in this innovation lies in that the acid used for reacting with the sodium present in the heavy residue is applied in a mole concentration corresponding to the salt concentration in the aqueous solution produced above the solvency limit. Thus, the salt generated by the reaction forms a suspension in the phase mixture which in turn maximizes density differences between the phases, facilitates separation and reduces organic matter contamination in the aqueous phase.

[0004] The process described in the previous patents presents a disadvantage in that it produces relatively low styrene yields and generates high salt content aqueous currents contaminated by organic compounds which require depuration, for example via biological degrading. In addition, phase separation is problematic.

DESCRIPTION OF THE INVENTION

[0005] The present invention refers to an improved propylene oxide and styrene monomer co-production procedure. The improvement consists in obtaining additional amounts of styrene and recovering 2-phenylethanol from a heavy residual current containing metals, mainly sodium, obtained in the form of a process by-product. According to the procedure that is the object of the invention, styrene yields are greater than those from prior art procedures; a fraction with a high 2-phenylethanol content, a compound used in the perfume industry, is simultaneously obtained; no highly metal salt and organic compound contaminated waters are generated, and a non-volatile, substantially metal-free residue is obtained that may serve as an appropriate fuel.

[0006] The known propylene oxide and styrene co-production process is described, for instance, in Spanish patents No. 314,229, 314,231, 307,877, 320,168, 323,754, 331,818, 334,098, 335,098, 343,579 and 365,624. In a first stage, ethyl benzene is made to react at high temperature with molecular oxygen in order to produce ethyl benzene hydroperoxide. The ethyl benzene hydroperoxide reacts with propylene to form propylene oxide and 1-phenylethanol. The mixture resulting from the epoxydizing reaction is normally submitted to alkaline rinsing and to a series of distillations designed to separate the various components: , propylene oxide, non-reacted ethyl benzene and 1-phenylethanol, leaving a heavy residue with a low content of sodium and other metals. The 1-phenylethanol current is dehydrated through known procedures, such as the one using p-toluenesulfonic acid as a catalyst for producing styrene monomer, as described, for example, in Japanese patent Kokai 8019247.

[0007] According to the present invention, the low-value sodium-containing heavy residue may be used directly, without previous metal removal, particularly sodium, as raw material for the production of styrene - a fraction with a relatively high 2-phenylethanol content, which is a compound used in the perfume industry -, and a heavy residue with a low sodium content, used as fuel.

[0008] According to the invention, the heavy residue containing sodium and other metals is dehydrated in the presence of a strong inorganic acid acting as a catalyst, at temperatures between approximately 150 and 250°C and pressures below the atmospheric pressure, preferably 50-400 mm.Hg, simultaneously vaporizing the light compounds, mainly styrene formed in the reaction and 2-phenylethanol; this organic distillation, representing

approximately 30 to 50% by weight of the heavy residue, is then fractionated by known methods, such as distillation, in order to recover pure styrene and a fraction containing relatively high amounts of 2-phenylethanol. This fraction can be used as a raw material for producing perfumery-degree 2-phenylethanol via known procedures. The residue of the non-volatile reaction is composed of heavy organic products, sodium salts and other inorganic acid metals and traces of the excess mineral inorganic acid. The metal salts may be easily separated from the organic products, e.g. by filtering, yielding a non-volatile organic residue practically exempt of sodium and other metals that is appropriate for fuel purposes.

[0009] Evidently, and according to the invention, the heavy residues from which most of the sodium and other metals have been removed by known procedures, such as treatment with aqueous acids and subsequent separation in phases, may be used as a raw material. However, this practice is normally not advisable in the context of the present invention because of the inconveniences associated to the type of treatment in question.

[0010] The strong inorganic acid used in treating the heavy residue containing sodium and other metals is preferably sulfuric acid. Other inorganic acids that may be used within the scope of the present invention include phosphoric, pyrophosphoric, polyphosphoric and fluorophosphoric acids, in addition to V_2O_5 solutions in polyphosphoric acids, etc. Mixtures of the above inorganic acids may also be used.

[0011] The strong inorganic acid must be used in an amount in excess of the stoichiometrical amount in order to allow it to react with all the sodium and other metals present in the heavy residue. It must be used in an amount above 1 acid equivalent per atom gram of sodium and other metals. The excess above the stoichiometrical amount is not critical. Normally, it is preferable to use the strong acid in a quantity high enough to provide, after reacting with the sodium and other metals, a free acid concentration in the reaction medium in the order of 0.001 to 1% by weight. With the use of smaller quantities, reaction is relatively slow; on the other hand, the use of larger quantities provides no additional advantage.

Example 1

[0012] The dehydration reaction of the heavy residue took place in a 50-liter glass reactor fitted with stirring means and connected at its upper portion to a water-cooled condenser. Vacuum was obtained from a water pump providing a constant pressure of 220 mm.Hg. 30 kg of heavy residues (1.0% by weight of sodium) and 0.7 kg of 96% sulfuric acid were initially added. Vacuum was applied at 220 mm.Hg, and the mixture was slowly heated to 220°C. Subsequently, continuous feeding of the heavy residue (1.0% by weight of sodium) and the 96% sulfuric acid was initiated in flow volumes of 10 kg/h and 0.23 kg/h, respectively, a non-volatile residue containing sodium sulfates and other metals being simultaneously extracted from the bottom in an average flow of 5.68 kg/h, and an organic distillate at an average flow of 4.32 kg/h being extracted from the top, comprising 44.4% styrene, 12.9% 2-phenylethanol, 1.8% acetophenone and 0.7% 1-phenylethanol, the balance containing mainly water and oxygenated compounds such as propylene oxide condensation products, ethers, etc.

[0013] With the practical application of this invention, styrene production is increased in 2.09%; this, in a commercial production facility capable of producing 500.000 tons of styrene per year, represents an added value of 888 million pesetas at current styrene prices.

Example 2

[0014] The reaction was performed in an installation similar to the one described in Example 1, save for the use of a 1-liter capacity reactor. Reaction temperature was 193°C, pressure was 140 mm.Hg. 302 gr/h of heavy residues (1.0% by weight of sodium) and 9.0 gr/h of 75% sulfuric acid were continuously added to the reactor. 127.3 gr/h (42.2% by weight of the heavy residues fed) of organic distillate and 18.5 gr/h water were obtained from the top of the reactor, and a current of 165.2 gr/h of non-volatile residues (54.7% by weight of the heavy residues fed) was obtained from the bottom of the reactor. The organic distillates were composed of 66.2% styrene, 22.0% 2-phenylethanol, 2.2% acetophenone, 1.8% 1-phenylethanol and 7.8% by weight of different oxygenated products, including propylene oxide condensation products, ether, etc.

Comparative Example 2

[0015] Example 2 was repeated exactly under the same conditions save for the replacement of the strong inorganic acid flow according to the invention, namely 9.0 gr/h, by a 21.9 gr/h flow of p-toluenesulphonic acid, an organic acid normally recommended for 1-phenylethanol dehydration. A yield was obtained amounting to 49.8% by weight in respect to the amount of heavy residue being fed, the composition of which was: 0.6% styrene, 25% 2-phenylethanol, 2.2% acetophenone, 18.0% 1-phenylethanol and 54.2% by weight of different oxygenated products, including propylene oxide condensation products, ether, etc.

[0016] This example illustrates the advantages of the heavy residue treatment according to the invention.

Example 3

[0017] The organic distillate current obtained in Example 1 was fractionated by distillation to recover 99.3%-rich styrene and a current containing 24.7% 2-phenylethanol usable to advantage as raw material for the recovery of 2-phenylethanol, perfumery degree, according to known procedures.

Example 4

[0018] The non-volatile residue containing sodium sulfates and other metals obtained in Example 1 were filtered at 80°C through a No. 4 porous glass plate, yielding a filtered matter containing < 0.1% sulfate ash usable as revalued fuel.

[0019] The above examples illustrate the invention and impose no limitation on it.

Claims

1. Improved propylene oxide and styrene monomer co-production procedure by oxidation of ethyl benzene with molecular oxygen to yield ethyl benzene hydroperoxide, epoxydizing propylene with said hydroperoxide to form propylene oxide and 1-phenylethanol, the epoxydizing product then being submitted to alkaline rinsing and the separation, though distillation, of the propylene oxide, the excess ethyl benzene and the 1-phenylethanol, producing a heavy residue containing sodium and other metals as a result of the alkaline rinsing of one or more of the process currents, and dehydrating the 1-phenylethanol to styrene, the improvement being **characterized by** the dehydration of said heavy residue containing sodium and other metals in the presence of a strong inorganic acid as a catalyst, at temperatures of 150-250°C and pressures below the atmospheric pressure, using the strong inorganic acid in an amount exceeding the stoichiometric amount in respect to the sodium and other metals contained in the residue.

2. Procedure according to claim 1, characteristic in that the strong inorganic acid is sulfuric acid.

3. Procedure according to any of the claims 1 and 2, characteristic in that the amount of strong inorganic acid is higher than the one corresponding to the stoichiometric ratio in respect to sodium and the other metals present in the heavy residue, preferably selected in such a manner that, after reacting with the sodium and other metals present in the heavy residue, there remains an excess of free inorganic acid with a concentration in the order of 0.001 and 1% by weight.

4. Procedure according to any of the claims 1 to 3, characteristic in that the dehydration reaction of the heavy residue containing sodium and other metals in the presence of a strong inorganic acid is conducted at an absolute pressure of 50-400 mm.Hg.

5. Procedure according to any of the claims 1 to 4, characteristic in that the organic distillates obtained by dehydrating the sodium-containing heavy residue with a strong inorganic acid are submitted to distillation to obtain pure styrene and a fraction with a relatively high 2-phenylethanol content.

6. Procedure according to any of the claims 1 to 5, characteristic in that the non-volatile residues obtained by dehydrating the heavy residue containing sodium and other metals in the presence of a strong inorganic acid are submitted to filtering in order to separate the inorganic salts and obtain a residue substantially free of sodium and other metals that can adequately be used as fuel.

Patentansprüche

1. Verbessertes Verfahren zur gemeinsamen Herstellung von Propylenoxid- und Styrolmonomeren durch das Oxidieren von Ethylbenzol mit molekularem Sauerstoff zum Erhalt von Ethylbenzolhydroperoxid, die Epoxidation von Propylen mit dem genannten Hydroperoxid zur Bildung von Propylenoxid und 1-Phenylethanol, wobei das Epoxidationsprodukt anschliessend einer alkalinen Spülung sowie der Abdestillierung des Propylenoxids, des Ethylbenzolüberschusses und des 1-Phenylethanols unterzogen wird, wodurch ein dichter Rückstand erhalten wird, welcher Natrium und andere Metalle als Ergebnis der alkalinen Spülung einer oder mehrerer Prozessströmungen enthält, und die Entwässerung des 1-Phenylethanols zu Styrol, wobei sich die Verbesserung auszeichnet durch die Entwässerung des genannten dichten, Natrium und andere Metalle enthaltenden Rückstands in Gegenwart einer starken anorganischen Säure als Katalysator bei Temperaturen von 150-250°C und bei unterhalb des Luftdrucks gelegenen Drücken, wobei die starke anorganische Säure in einer über der stöchiometrischen Menge in Bezug auf das Natrium und die anderen im Rückstand enthaltenen Metalle liegenden Menge verwendet wird.

2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** die starke anorganische Säure Schwefelsäure ist.

3. Verfahren nach einem der Ansprüche 1 und 2, **dadurch gekennzeichnet, dass** die Menge der starken anorganischen Säure höher als die dem stöchiometrischen Verhältnis zum Natrium und den anderen im dichten Rückstand vorhandenen Metalle entsprechenden Menge ist und bevorzugt derart gewählt wird, dass nach der Reaktion mit dem Natrium und den anderen im dichten Rückstand vorhanden Metallen ein Überschuss an freier anorganischer Säure in einer Konzentration im Bereich von 0,001 und 1 Gewichtsprozent verbleibt.

4. Verfahren nach einem der Ansprüche 1 bis 3, **dadurch gekennzeichnet, dass** die Entwässerungsreaktion des dichten, Natrium und andere Metalle enthaltenden Rückstands in Gegenwart einer starken anorganischen Säure bei einem absoluten Druck von 50-400 mm.Hg durchgeführt wird.

5. Verfahren nach einem der Ansprüche 1 bis 4, **dadurch gekennzeichnet, dass** die durch die Entwässerung des dichten, Natrium enthaltenden Rückstands mit einer starken anorganischen Säure erhaltenen organischen Destillate einer Destillation zum Erhalt reinen Styrols und einer Fraktion mit einem relativ hohen Gehalt an 2-Phenylethanol unterzogen werden.

6. Verfahren nach einem der Ansprüche 1 bis 5, **dadurch gekennzeichnet, dass** die durch die Entwässerung des dichten, Natrium und andere Metalle enthaltenden Rückstands in Gegenwart einer starken anorganischen Säure erhaltenen nicht flüchtigen Rückstände einer Filtration unterzogen werden, um die anorganischen Salze abzutrennen und einen im wesentlichen von Natrium und anderen Metallen freien Rückstand zu erhalten, der adäquat als Brennstoff verwendet werden kann.

Revendications

1. Procédé amélioré de coproduction de monomères d'oxyde de propylène et de styrène par le moyen de l'oxydation d'éthylbenzène avec de l'oxygène molléculaire pour produire de l'hydropéroxyde d'éthylbenzène, l'époxydation du propilène avec ledit hydropéroxyde pour former de l'oxyde de propylène et 1-phényléthanol, le produit de l'époxydation étant soumis postérieurement à un rinçage alcalin et à la séparation, par le moyen de distillation, de l'oxyde de propylène, l'excès d'éthylbenzène et le 1-phényléthanol, en produisant un résidu dense qui contient du sodium et d'autres métaux résultant du rinçage alcalin d'un ou de plusieurs des courants du processus, et la déshydratation du 1-phényléthanol à styrène, étant l'amélioratalon **caracterisée par** la déshydratation dudit résidu dense qui contient du sodium y d'autres métaux en présence d'un acide inorganique fort comme catalyseur, à des temperatures de 150-250°C et à des pressions au dessous de la pression atmosphérique, en utilisant l'acide inorganique fort en une quantité supérieure à la quantité stoechiométrique par rapport au sodium et aux autres métaux contenus dans le résidu.

2. Procédé selon la revendication 1, **caractérisé en ce que** l'acide inorganique fort est l'acide sulphurique.

3. Procédé selon quelconque des revendications 1 et 2, **caractérisé en ce que** la cantité d'acide inorganique fort es supérieure à celle qui correspond à la relation stoechiométrique par rapport au sodium et aux autres métaux présents dans le résidu dense, et elle est sélectionnée de préférence de façon à ce que, après la réaction avec le sodium et les autres métaux présents dans le résidu dense, il continue d'éxister un excès d'acide inorganique libre dans une concentration de l'ordre du 0,001 y du 1% en poids.

4. Procédé selon quelconque des revendications 1 à 3, **caractérisé en ce que** la réaction de déshydratation du résidu dense qui contient du sodium et d'autres métaux en présence d'un acide inorganique fort est rélisée à une pression absolue de 50-400 mmHg.

5. Procédé selon quelconque des revendications 1 à 4, **caractérisé en ce que** les distillés organiques obtenus par le moyen de la déshydratation du résidu dense qui contient du sodium avec un acide inorganique fort sont soumis à une distillation pour obtenir de styrène pur et une fraction avec une teneur relativement grande de 2-phéniléthanol.

6. Procédé selon quelconque des revendications 1 à 5, **caractérisé en ce que** les résidus non volatiles obtenus par le moyen de la déshydratation du résidu dense qui contient du sodium y d'autres métaux en présence d'un acide organique fort sont soumis à une filtration pour séparer les sels inorganiques et obtenir un résidu substantiellement sans sodium et d'autres métaux qui puisse être utilisés convenablement comme combustile.